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AN OXIDATION REACTION OF $Cl_3Sn\text{-}Mn(CO)_5$ WITH $KMnO_4$

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A reaction of $Cl_3Sn\text{-}Mn(CO)_5$ with $KMnO_4$ in a mixed solvent afforded $ClMn(CO)_5$ and a tin-hydroxo compound. The manganese atom in $Cl_3Sn\text{-}Mn(CO)_5$ is oxidized mildly from 0 to +1 in oxidation number by $KMnO_4$.

It is well recognized that metal carbonyl derivatives are generally unstable and sometimes oxidized to metal oxides with oxygen and/or strong oxidizing reagents in organic solvents. The present paper, however, reports that the $Mn(CO)_5$ moiety of $Cl_3Sn\text{-}Mn(CO)_5$ is left unaffected and $ClMn(CO)_5$ is afforded in a reaction of $Cl_3Sn\text{-}Mn(CO)_5$ with $KMnO_4$.

In the due course of the ^{55}Mn-NMR measurements for a series of $L_{3-x}X_xSn\text{-}Mn(CO)_5$ compounds (x = 0-3),[1] a 0.5 mol tetrahydrofuran solution (4 cc) of $Cl_3Sn\text{-}Mn(CO)_5$ was accidentally admixed with a 10 % aqueous solution (2 cc) of $KMnO_4$ in a sealed glass tube, $KMnO_4$ was used as an external standard for the ^{55}Mn-NMR measurements. A purple color due to $KMnO_4$ was gradually disappeared and a transparent orange-yellow solution was obtained. After the solution was kept standing in a refrigerator for a month, orange-yellow crystals were precipitated. The solution was kept standing in the refrigerator over one year further to complete the precipitation of the crystals. The crystals were filtered out and dried in vacuo.[2] (Yield: 80 mg) The filtrate was concentrated to half a volume under a reduced pressure. The supernatant oily substance was separated with a syringe. (Yield: 0.5 cc) The crystal was subjected to mass spectrum measurements.[3] The mass spectrum (70 eV) showed the parent peaks at m/e = 232 and 230, which were assignable to a $ClMn(CO)_5^+$ ion, and a series of peaks due to $ClMn(CO)_{5-x}^+$ ions (x = 2-5) and $Mn(CO)_{5-x}^+$ ions (x = 0-5). The fragmentation pattern resembles that of the authentic $ClMn(CO)_5$.[4] The carbon analysis is a further evidence that the crystal is $ClMn(CO)_5$: Found; C = 26.18 %, Calcd. for C_5ClMnO_5; C = 26.00 %.

The oily substance was subjected to infrared spectrum measurements. The spectrum showed the absorptions at 3300 cm^{-1} (vs) and at 600 cm^{-1} (very broad). The peak at 3300 cm^{-1} is assignable to a OH stretching vibration, and the peak at 600 cm^{-1} is assignable to a Sn-O stretching vibration.[5,6] Therefore, the oily substance is/, or contains, a tin-hydroxo complex.

The oxidation number of the manganese atom is 0 for $Cl_3Sn-Mn(CO)_5$[1,7] and +1 for $ClMn(CO)_5$.[1,8] The manganese atom is mildly oxidized by $KMnO_4$ in this reaction. The result led us to conclude that it is possible to oxidize mildy metal carbonyl derivatives by strong oxidizing agents such as $KMnO_4$ under an appropriate condition.

The mechanism of the rearrangement of the chlorine atom from the tin atom to the manganese atom has not yet been clarified. No such oxidation reaction of metal-metal bonds has thus far been found in the literature, though similar rearrangement of the phenyl group of $Ph_3Sn-Mn(CO)_5$ from the tin atom to the manganese atom has been reported by Lewis et al. on electron impact.[9] Further details of this oxidative rearrangement mechanism will be reported together with results on other compounds.

References and footnotes

1) S. Onaka, T. Miyamoto and Y. Sasaki, Bull. Chem. Soc. Japan, 44, 1851 (1971).

2) The reaction should be performed with caution; inflammable gasses are evolved in the reaction.

3) The author's thanks are due to Mr. Yasuo Maki, Government Industrial Research Institute, Nagoya, for his kind measurements of the mass spectra.

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